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PCT	То:
NOTIFICATION OF ELECTION (PCT Rule 61.2)	Assistant Commissioner for Patents United States Patent and Trademark Office Box PCT Washington, D.C.20231 ETATS-UNIS D'AMERIQUE
Date of mailing (day/month/year) 04 October 2000 (04.10.00)	in its capacity as elected Office
International application No. PCT/NO00/00034	Applicant's or agent's file reference KOH102104
International filing date (day/month/year) 03 February 2000 (03.02.00)	Priority date (day/month/year) 04 February 1999 (04.02.99)
Applicant PRUCKNER, Franz	
The designated Office is hereby notified of its election made in the demand filed with the International Preliminar 23 August 200 in a notice effecting later election filed with the International Preliminar 23 August 200	ry Examining Authority on: 00 (23.08.00)
2. The election X was was not was not made before the expiration of 19 months from the priority Rule 32.2(b).	date or, where Rule 32 applies, within the time limit under
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Manu Berrod

Telephone No.: (41-22) 338.83.38

Form PCT/IB/331 (July 1992)

Facsimile No.: (41-22) 740.14.35



PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicar		_	it's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
Internati	lonal s		ation No.	International filing date (day/mont	th/year) Priority date (day/month/year)
PCT/N		• •		03/02/2000	04/02/1999
C23F1	13/02		t Classification (IPC) or	national classification and IPC	
• •		OR	AS et al.		
an	d is t	rans	mitted to the applica	nt according to Anticle 36.	ed by this International Preliminary Examining Authority
2. Th	nis RE	POI	RT consists of a total	of 4 sheets, including this cover a	sheet.
⊠ Th	bee (se	en ar e Ru	nended and are the	basis for this report and/or sheets n 607 of the Administrative instruct	the description, claims and/or drawings which have containing rectifications made before this Authority tions under the PCT).
3. Th	nia rep I	_	contains indications Basis of the report	relating to the following items:	
	11		Priority		
	Ш		Non-establishment	of opinion with regard to novelty, in	nventive step and industrial applicability
	IV		Lack of unity of inve	ention	
	V	×		nt under Article 35(2) with regard to nations suporting such statement	o novelty, inventive step or Industrial applicability;
	٧i		Certain documents	, =	
	VII		-	ne international application	
<u>الم</u>	/111	Ø		s on the international application	
Date of	ndue i	isslo	n of the demand	Date o	of completion of this report
23/08	/200)		26.04.	.2001
			address of the internal	lonal Author	rized officer
	<u>M</u>	Euro D-80	pean Patent Office 298 Munich 49 89 2399 - 0 Tx: 52	Mizer	ra, E
			+49 89 2389 - 4465	·	hone No. +49 89 2399 8580



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NO00/00034

		is of the report				
1.	the r	receiving Office in res	nts of the international applic ponse to an invitation under is report since they do not c	Article 14 are	referred to in this rep	oort as "originally filed"
	1-8	as	originally filed			
	Clair	ms, No.:				
	1-4	as	received on	14/04/2001	with letter of	04/04/2001
2.	With	regard to the la ng ua uage in which the inte	i ge, all the elements marked ernational application was fil	i above were a led, unless oth	ivailable or fumished erwise indicated und	i to this Authority in the er this item.
	The	se elements were ava	allable or furnished to this Au	uthority in the f	ollowing language:	, which is:
		the language of a tra	nslation furnished for the pu	rposes of the i	nternational search	(under Rule 23.1(b)).
		the language of publi	ication of the international a	pplication (und	er Rule 48.3(b)).	
		the language of a tra 55.2 and/or 55.3).	nslation furnished for the pu	irposes of inter	national preliminary	examination (under Rule
3.	With inter	n regard to any nucle mational preliminary e	otide and/or amino acid se examination was carried out	equence disclo	sed in the internation of the sequence listin	nal application, the g:
		contained in the inter	mational application in writte	en form.		
		filed together with the	e international application in	computer read	dable form.	
		fumished subsequer	ntly to this Authority in written	n form.		•
		furnished subsequer	itly to this Authority in comp	uter readable f	orm.	
			he subsequently furnished w lication as filed has been fui		e listing does not go	beyond the disclosure in
		The statement that the listing has been furnitude.	ne information recorded in c ished.	omputer reada	ble form is identical	to the written sequence
4.	The	amendments have re	esulted in the cancellation of	f:		
		the description,	pages:			
		the claims,	Nos.:			
		the drawings,	sheets:			

5. This report has been established as if (some of) the amendments had not been made, since they have been

considered to go beyond the disclosure as filed (Rule 70.2(c)):







International application No. PCT/NO00/00034

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

- 6. Additional observations, if necessary:
- V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- 1. Statement

Novelty (N)

Yes:

Claims 1-4

No:

Claims

Inventive step (IS)

Yes:

Claims 1-4

No:

Claims

Industrial applicability (IA)

Yes:

Claims 1-4

Claims No:

2. Citations and explanations see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made: see separate sheet





INTERNATIONAL PRELIMINARY International EXAMINATION REPORT - SEPARATE SHEET

International application No. PCT/NO00/00034

AS TO BOX V:

- 1. Claim 1 differs from the teaching of EP-A-0 581 433 in that the coating composition comprises water soluble inorganic silicate. With respect to US-A-4035 265, cited in the application, the difference consists in the use of the coating composition, which also comprises an impregnation agent, for the protection of concrete against corrosion, whereas the cited document teaches the use for heating purposes (which inherently requires a different composition, e.g. with respect to the amount of dispersed graphite).
- 2. Claim 1 and claims 2-4, depending thereon, meet therefore the requirements of Art.33(2) PCT.
- 3. The claimed use of the coating composition involves a petrification of the substrate, caused by the impregnation with the water soluble silicates.
 Delamination effects due to acidification of the interphase coating/concrete are thus strongly reduced. This supports the required inventive step.
- 4. Claims 1-4 meet therefore also the requirements of Art.33(3) PCT.

AS TO BOX VIII:

1. The description should be adapted to the amended claims.





CLAIMS

- 1. Use of a coating composition comprising graphite dispersed in a curable mineralic binder, in the form of water glass or another water soluble inorganic silicate, a dispersion agent, an impregnation agent, optionally together with conventional additives for cathodic protection, as well as optionally an outer ionic reservoir, for the protection of concrete against corrosion.
- 2. Use according to claim 1, wherein the composition, as additives contains additives that function as curing agents.
- 3. Use according to claims 1-2, wherein the impregnation is carried out with a silane/siloxane solution of low viscosity.
- 4. Use according to claims 1-3, wherein the composition is applied for cathodic protection of reinforcement in concrete in connection with quay constructions, bridges, bridge piers and similar constructions.

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PCT





INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

51) International Patent Classification 7: C23F 13/02	A1	11) International Publication Number: WO 00/46421 43) International Publication Date: 10 August 2000 (10.08.00
(21) International Application Number: PCI/NOC (22) International Filing Date: 3 February 2000 (C (30) Priority Data: 19990509 4 February 1999 (04.02.99) (71) Applicant (for all designated States except US): PROMAS [NO/NO]; P.O. Box 75, N-3050 Mjöndalen (R (72) Inventor; and (75) Inventor/Applicant (for US only): PRUCKNET [NO/NO]; Övre Hön Terrasse 8b, N-1370 Asker (74) Agent: HANSSEN, Kari, Olaug; Bryn & Aarflot AS, 449 Sentrum, N-0104 Oslo (NO).	17ECT(NO).	BR. BY. CA, CH. CN, CR, CU, CZ, DE, DR, DM, ER ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JI KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RI SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KI LS, MW, SD, SL, SZ, TZ, UG, ZW). Eurasian patent (AA AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (A' BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LI MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE

(57) Abstruct

A method is described for the electrochemical protection of reinforcement in concrete in hursh environments, for instance in contact with, or in close proximity to, seawater. On concrete a composition comprising graphite dispersed in a curable mineralic binder in the form of water glass or another water-soluble inorganic silicate, a dispersion agent, optionally together with conventional additives is applied. The application is performed by spraying or brushing. An impregnation is optionally performed, either concurrent with the application of the composition or thereafter. If necessary a post treatment is performed. Further, the use of the composition for electrochemical protection of reinforcement in concrete in connection with, for instance, quay constructions, bridges, bridge piers and similar constructions is described.

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C23F 13/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL, EDOC, JAPIO

Į	C. DOCUMENTS	CONSIDERED TO	O BE RELEVANI	

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0581433 A1 (ZENECA INC.), 2 February 1994 (02.02.94), page 4, line 30 - page 7, line 23, claims 1,4,8, abstract	1-8
A	US 5366600 A (LUC B.J. WESTHOF ET AL), 22 November 1994 (22.11.94), column 1, line 49 - column 2, line 15; column 3, line 19 - column 5, line 22, abstract	1-8
Ä	GB 2140456 A (TAYWOOD ENGINEERING LIMITED (UNITED KINGDOM)), 28 November 1984 (28.11.84), page 1, line 46 - line 72, figure 1, abstract	1-8

X See patent family annex.

- Special categories of cited documente
- document defining the general state of the art which is not considered to be of particular relevance
- erlier document but published on or after the international filing date
- document which may throw doubts on priority claim(s) or which is cited to exabilish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other
- document published prior to the international filing date but later than the priority date claimed
- later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the elaimed invention cannot be considered novel or cannot be considered to involve an inventive stop when the document is taken alone
- document of particular relevance: the claimed invention extinot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of mailing of the international search report Date of the actual completion of the international search 10 -05- 2000 4 May 2000 Authorized officer Name and mailing address of the ISA/

Swedish Patent Office

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Ingrid Grundfelt/MP Telephone No. +46 8 782 25 00

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C (Continu	ation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Sategory*	Citation of document, with indication, where appropriate, of the releva	int passages	Relevant to claim No.
A	EP 0730046 A1 (EKO D.O.O.), 4 Sept 1996 (04.09 page 2, line 36 - page 3, line 47, abstract	.96),	1-8
1			
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INTERNATION EARCH REPORT

02/12/99

ational application No. PCT/NO 00/00034

	stent document in search report		Publication date		Patent family member(s)	•	Publication date
EP	0581433	A1 .	02/02/94	AT AU AU CA DE ES JP US US	4139293 2099955 69300801 2082594 6322566	T A A	15/12/95 24/11/94 27/01/94 22/01/94 01/08/96 16/03/96 22/11/94 15/11/94 11/07/95
us	5366600	A	22/11/94	US AT AU AU CA DE EP JP	5501819 138358 651170 1086692 2061085 69210854 0499439 5078159	A A D,T A,B	26/03/96 15/06/96 14/07/94 20/08/92 13/08/92 31/10/96 19/08/92 30/03/93
GB	2140456	Α	28/11/84	NON	E		
EP	0730046	A1	04/09/96	BA HR NO SI	96081 960098 960841 9500064	A A	02/08/99 31/12/97 02/09/96 31/10/96



PCT REQUEST

KOH102104

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0	For receiving Office use only	
0-1	International Application No.	PCT/NO 0 0 0 0 0 3 4
0-2	International Filing Date	
		- 3 FEB. 2000 (03 02 2000)
)-3	Name of receiving Office and "PCT	[25]
	International Application*	PATENTSTYRET
	1	Other for dat industricity minusers FCT International application
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.90
		(updated 15.12.1999)
0-5	Petition	
	The undersigned requests that the present international application be	
	processed according to the Patent	
	Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Norwegian Patent Office (RO/NO)
0-7	Applicant's or agent's file reference	KOH102104
U- <i>1</i>	1	1101110111011
• •	Title of invention	CONDUCTIVE MINERALIC COATING FOR
• •	Title of invention	
• •	Title of invention	CONDUCTIVE MINERALIC COATING FOR
<u> </u>	Title of invention Applicant	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF
1		CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF
II II-1	Applicant	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE
II II-1 II-2	Applicant This person is:	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only
II II-1 II-2 II-4 II-5	Applicant This person is: Applicant for	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US
 -1 -2	Applicant This person is: Applicant for Name	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US PROTECTOR AS P.O.Box 75
 	Applicant This person is: Applicant for Name	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US PROTECTOR AS P.O.Box 75 N-3050 Mjöndalen
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 	Applicant This person is: Applicant for Name Address: State of nationality State of residence Applicant and/or inventor	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US PROTECTOR AS P.O.Box 75 N-3050 Mjöndalen Norway NO NO applicant and inventor
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 	Applicant This person is: Applicant for Name Address: State of nationality State of residence Applicant and/or inventor This person is: Applicant for Name (LAST, First)	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US PROTECTOR AS P.O.Box 75 N-3050 Mjöndalen Norway NO NO applicant and inventor US only PRUCKNER, Franz
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 	Applicant This person is: Applicant for Name Address: State of nationality State of residence Applicant and/or inventor This person is: Applicant for Name (LAST, First)	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US PROTECTOR AS P.O.Box 75 N-3050 Mjöndalen Norway NO NO applicant and inventor US only PRUCKNER, Franz Övre Hön Terrasse 8b N-1370 Asker
	Applicant This person is: Applicant for Name Address: State of nationality State of residence Applicant and/or inventor This person is: Applicant for Name (LAST, First) Address:	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US PROTECTOR AS P.O.Box 75 N-3050 Mjöndalen Norway NO NO applicant and inventor US only PRUCKNER, Franz Övre Hön Terrasse 8b N-1370 Asker Norway
	Applicant This person is: Applicant for Name Address: State of nationality State of residence Applicant and/or inventor This person is: Applicant for Name (LAST, First)	CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE applicant only all designated States except US PROTECTOR AS P.O.Box 75 N-3050 Mjöndalen Norway NO NO applicant and inventor US only PRUCKNER, Franz Övre Hön Terrasse 8b N-1370 Asker

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IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the	agent
	competent International Authorities as:	
IV-1-1	Name (LAST, First)	HANSSEN, Kari, Olaug
V-1-2	Address:	BRYN & AARFLOT AS
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		Norway
V-1-3	Telephone No.	+47 22 00 31 00
V-1-4	Facsimile No.	+47 22 00 31 31
V-1-5	e-mail	email@baa.no
V	Designation of States	
V-1	Regional Patent	AP: GH GM KE LS MW SD SL SZ TZ UG ZW and
	(other kinds of protection or treatment, if any, are specified between parentheses	any other State which is a Contracting
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<i>V</i> -2	(other kinds of protection or treatment, if	EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT AE AL AM AT AU AZ BA BB BG BR BY CA
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<i>J-</i> 2	(other kinds of protection or treatment, if any, are specified between parentheses	EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT AE AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM EE ES FI GB
V-2	(other kinds of protection or treatment, if any, are specified between parentheses	EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT AE AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG
V-2	(other kinds of protection or treatment, if any, are specified between parentheses	EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT AE AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG

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V-5	Descriptions Designation Statement	· · · · · · · · · · · · · · · · · · ·	
V-5	Precautionary Designation Statement In addition to the designations made		
	under items V-1, V-2 and V-3, the		
	applicant also makes under Rule 4.9(b)		
	all designations which would be		
	permitted under the PCT except any		
	designation(s) of the State(s) indicated		
	under item V-6 below. The applicant		
	declares that those additional		•
	designations are subject to confirmation		
	and that any designation which is not		•
	confirmed before the expiration of 15		$\Psi_{ij} = \Psi_{ij} + \Psi$
	months from the priority date is to be		
	regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	Exclusion(s) from precautionary	MONTE	
V-0	designations	NONE	
VI-1	Priority claim of earlier national		
,	application		
VI-1-1	Filing date	04 February 1999 (04	02 1000)
		<u> </u>	.02.1333)
VI-1-2	Number	1999 0509	
VI-1-3	Country	NO	
VI-2		110	<u> </u>
V1-2	Priority document request	l a	
	The receiving Office is requested to prepare and transmit to the International	VI-1	
	Bureau a certified copy of the earlier		
	application(s) identified above as	·	. :
	item(s):	·	•
VII-1	International Searching Authority	Swedish Patent Offic	A (TCA/CE)
• • • •	Chosen	Swedish Facent Offic	e (IBA/BE)
VII-2	Request to use results of earlier		·
	search; reference to that search		
VII-2-1	Date	11 October 1999 (11.	10.1999)
VII-2-2	Number	1999 0509	• • • •
VII-2-3	Country (or regional Office)	NO	· *
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	4	_
VIII-2	Description	 	
	Description	6	-
VIII-3	Claims	2	-
VIII-4	Abstract	1	102104abs.txt
		·	102104abs.txt
VIII-5	Drawings	0	-
VIII-7	TOTAL	13	<u> </u>
	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	 -
VIII-9	Separate signed power of attorney		1-
VIII-16	PCT-EASY diskette		<u> </u>
VIII-10	PCT-EAST diskette	-	diskette
VIII-18	Figure of the drawings which should accompany the abstract		
VIII-19	Language of filing of the international application	Norwegian	,
IX-1	Signature of applicant or agent	Tan Olang Hangen	
IX-1-1	Name (LAST, First)	HANSSEN, Kari, Olaug	ī
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PCT REQUEST

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10-1	Date of actual receipt of the purported international application	- 3 FEB. 2000 (03.02	(Ω)
10-2	Drawings:		
10-2-1	Received		
10-2-2	Not received		
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application		
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)		
10-5	International Searching Authority	ISA/SE	
10-6	Transmittal of search copy delayed until search fee is paid	total and the second	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by	0 6 MARCH 2000	
	the International Bureau	U6 MARCH 2000	(n e us uu)

LEDENDE MINERALSK PÅFØRINGSMIDDEL FOR ELEKTROKJEMISK KORROSJONSBESKYTTELSE AV STÅLALARMERING I BETONG

Foreliggende oppfinnelse vedrører et ledende mineralsk påføringsmiddel anvendt for elektrokjemisk korrosjonsbeskyttelse av stålarmering i betong.

Nærmere bestemt vedrører oppfinnelsen en fremgangsmåte for elektrokjemisk beskyttelse av armering i betong i utsatte miljøer, samt en anvendelse av et ledende påføringsmiddel for å beskytte armering i betong i slike miljøer.

Det har i mange tiår vært kjent at uorganiske bindemidler, som sement, spesielt portlandsement, som har alkaliske egenskaper, beskytter jernholdige metaller mot korrosjon. Grunnet denne korrosjonsbeskyttende effekten har det vært mulig å fremstille armert betong hvor stålet er innstøpt i betong, og det har ikke vært påkrevet å påføre noen beskyttelse, for eksempel i form av beskyttende maling, på stålet.

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Den korrosjonsbeskyttende effekt av sement skyldes dannelsen av kalsiumhydroksyd under hydratiseringen som fører til en pH-verdi på 12 og høyere inne i sementpastaen.

Når sement karbonatiseres, hvilket betyr at karbondioksyd fra luften reagerer med kalsiumhydroksyd, kan pH-verdien synke flere pH-enheter. Ved pH-verdier under 9 begynner armeringsstålet å korrodere.

Korrosjonen akselereres ved sprekkdannelse i bygningsmaterialet så vel som ved innvirkningen av klorider fra kontaminerte aggregater, salter for av-ising, luftforurensning og sjøvann.

En fremgangsmåte for å bekjempe korrosjon av stål i betong er å polarisere stålet katodisk (katodisk beskyttelse, elektrokjemisk kloridfjernelse, elektrokjemisk realkalisering), hvor stålet er katoden, eller den negative polen, og en ytre anode er den positive polen. Som slike ytre anoder har det vært anvendt Ti-nett, -tråder eller –staver belagt med blandede metalloksyder, elektrisk ledende asfalt, flamme-sprayet sink eller titan og ledende malinger. En ledende maling har to vesentlige fordeler. For det første medfører den ikke stor ekstravekt for konstruksjonen, hvilket kan være et problem for slanke konstruksjoner fra et statisk synspunkt. For det andre kan den ledende malingen gi en svært god strømfordeling.

De eksisterende malingene er hovedsakelig komposittmaterialer med en polymer (akrylater, lateks, polystyren og lignende) som et filmdannende binde-

middel (bæremiddel) og grafitt som fyllstoffmateriale, såkalte skjelettledere. Bindemiddelet i disse kjente malingene har i praksis ingen ledningsevne, men er tilstede i produktet som et bærermateriale som hefter til betongen. Anoden består derved av grafittfibre eller –korn innbakt i en isolator. Ledningen vil foregå via disse kontaktpunktene og det kan derfor forventes en stor belastning i disse overgangene grafitt/grafitt. Dette vil i stor grad begrense anodens ledningsevne. En konsekvens av den høye overgangsmotstanden en slik anode får mot betongunderlaget er at høyere spenning må benyttes. Derved får man elektrolyse, hvorved kontaktpunktene oksyderer og anoden "dør". Det skal i tillegg bemerkes at plastbaserte bindemidler er diffusjonshindrende og derved ikke anses å ha noen holdbarhet i utsatte miljøer. Videre vil malingen miste sin adhesjon til betongbasisen på grunn av de elektrokjemiske reaksjonene som finner sted ved grenseflaten mellom betong og maling, hvilket fører til svikt av den elektrokjemiske behandlingen.

På betong i utsatte miljøer, for eksempel i kontakt med, eller i nærheten av, sjøvann forekommer det ofte store korrosjonsskader. Likeledes må det i slike omgivelser stilles nye krav til anodematerialene, idet også disse vil undergå sterk korrosjon i et slikt miljø. Som et eksempel kan her nevnes kaianlegg som er utsatt for armeringskorrosjon. Den eneste muligheten for å løse dette problemet har vært katodisk beskyttelse, fortrinnsvis med Ti-nett innstøpt i sprøytebetong installert under kaien. Dette er en omstendelig og kostnadskrevende prosedyre. Delaminering av disse lagene forekommer i utstrakt grad. Det har vist seg umulig å anvende de kjente malingssystemene i slike våte eller fuktige miljøene. Dette fordi det opptrer omfattende delaminering og/eller blæredannelse på grunn av den tilstedeværende fuktigheten, og det vil også ofte være problematisk å oppnå tilstrekkelig heft allerede ved den innledende påføringen av malingsfilmen.

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Fagmiljøet har følgelig trukket den konklusjon at ledende maling ikke kan anvendes under slike utsatte og fuktige betingelser. Dette har ført til at innstøping av ledende nett i dag anses som den eneste, om enn utilfredsstillende, løsningen.

Hensikten med foreliggende oppfinnelse er å gi anvisninger til en ny løsning på dette problemet, nærmere bestemt å tilveiebringe en enkelt påførbar, mekanisk og elektrokjemisk stabil anodeløsning som også fungerer godt i fuktig miljø og nær, eller i kontakt med, sjøvann.

For løsning av dette problemet har oppfinneren sett nødvendigheten av å unngå filmdannende påføringsmidler, og har dermed kommet frem til et enkelt og meget velegnet system.

Det er kjent at silikatbaserte mineralske malinger reagerer med substratet (puss, betong, naturstein osv.) ved forsteining (petrification). Dette betyr at de vannoppløselige silikatene penetrerer mineralsubstratet hvorpå de er påført og danner en kjemisk, mikrokrystallinsk binding med dette, i motsetning til filmdannende malinger som danner en overflatehud.

påføres på vegger og lignende for oppvarmingsformål. Malingssammensetningen inneholder karbonpartikler samt flak av grafitt, videre et herdbart bindemiddel som kan være et uorganisk silikatbindemiddel, et organisk ammoniumsilikatbindemiddel eller for eksempel et harpiksbindemiddel som er oppløselig i organisk oppløsningsmiddel. På grunn av den tilsiktede anvendelsen som oppvarmingskilde inneholder denne malingen store mengder grafitt/karbonpartikler. Også ved flere andre trekk, som vil bli nærmere omtalt nedenfor, adskiller dette systemet seg fra foreliggende oppfinnelse.

Foreliggende oppfinnelse tilveiebringer følgelig en fremgangsmåte for elektrokjemisk beskyttelse av armering i betong i utsatte miljøer, for eksempel i kontakt med, eller i nærheten av, sjøvann, kjenntegnet ved at betongen påføres et middel omfattende grafitt dispergert i vannglass eller et annet uorganisk silikat, et dispersjonsmiddel samt eventuelt vanlige tilsetningsstoffer, ved påsprøyting eller bestrykning, og en impregnering gjennomføres eventuelt, enten samtidig med påføringen av det ovenfor nevnte middelet eller etter dette. Eventuelt kan det deretter gjennomføres en etterbehandling.

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Ved at det ved fremgangsmåten ifølge oppfinnelsen ikke dannes noen film, men snarere en impregnering, opptrer ikke de omtalte problemene med heft, delaminering og blæredannelse. Den mineralske blandingen vil penetrere det ytre betonglaget og danne et gellignende materiale i porene og på betongoverflaten, og vil derfor, når vannet fordamper, adhere sterkt til betong, murverk og natursteinoverflater. Derved vil overgangsmotstanden mellom anode og betong bli lavest mulig.

Når det katodiske anlegget startes vil spenningsfeltet som oppstår medføre migrering av ioner hvilket fører til ytterligere herding og styrker anoden. På grunn

av styrken av det herdede påføringsmiddelet vil grafittpartiklene være fullstendig immobilisert og fungere som et veletablert skjelett slik at det oppnås en meget ledende anode for elektrokjemiske behandlinger. Dette medfører at det ved fremgangsmåten ifølge foreliggende oppfinnelse kan opereres med høyere strømtettheter enn ved de tidligere kjente malingsbeleggene. Videre vil de høyere strømtetthetene oppnås ved lavere spenning enn ved kjente anodetyper. Dette vil i sterk grad påvirke anodens levetid i positiv retning.

Siden oppløsningen/dispersjonen av de mineralske forbindelsene anvendt i påføingsmiddelet er sterkt alkaliske reduseres delamineringseffektene ved surgjøring av grenseflaten påføringsmiddel/betong ved den elektrokjemiske prosessen ved anoden i sterk grad. En anode ifølge kjent teknikk med lateks-akrylbindemiddel vil derimot over tid miste heft på grunn av denne prosessen. Dette trekket er av meget stor betydning, idet det vil dannes syre ved anodebetong ved katodisk beskyttelse. Ved det alkaliske påføringsmiddelet ifølge oppfinnelsen oppnås et reservoar mot syredannelse, hvilket er meget ønskelig idet syre, som kjent, løser betong.

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En annen fordelaktig effekt ved denne typen anode for katodisk beskyttelse er at det elektriske feltet vil trekke alkaliioner fra påføringsmiddelet ved elektroforetisk bevegelse. Dette fører til økende polymerisasjonsgrad av silikatgelen som derved blir stadig mer forstenet og bestandig. Etter en viss tid er det dannet en fullstendig uoppløselig matriks av silikat-hydrogel som bindemiddel. Dette medfører at silikatpåføringsmiddelet anvendt i fremgangsmåten ifølge oppfinnelsen er utmerket egnet som anode ved katodisk beskyttelse av meget fuktige strukturer, som for eksempel undersiden av kaianlegg, havneanlegg eller bropilarer hvor de vanlige malingene hittil har sviktet.

Påføringsmidlet kan ved fremgangsmåten ifølge oppfinnelsen enkelt sprayes på betongoverflaten ved hjelp av vanlige malingspistoler eller det kan strykes på betongoverflaten ved hjelp av konvensjonelle redskaper.

Som nevnt ovenfor kan det, om ønsket, tilsettes vanlige tilsetningsstoffer i påføringsmiddelet som anvendes. Herunder kan også herdemidler tilsettes. Som herdemiddel kan det for eksempel anvendes fosfater av aluminium, jern, sink, bly osv., flerverdige estere eller ammonium-, amin- eller amidforbindelser. Som omtalt tidligere vil strømgjennomgang i den påførte impregneringen i seg selv bevirke tilstrekkelig herding. Det kan imidlertid tenkes tilfeller hvor tilsats av herdemiddel

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vil være fordelaktig, for eksempel før strømtilførsel er mulig eller før annen beskyttelse er på plass.

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Ifølge en mulig utførelsesform av foreliggende oppfinnelse kan påføringsmidlet tilsettes en katalysator. Som katalysator kan det for eksempel anvendes edelmetaller, heterocykliske forbindelser med interstitielle metallatomer, osv.. Det er funnet at doping av grafitten med edelmetaller forhindrer oksydasjon av grafitt. Påføringsmiddelet inneholdende grafitt dopet med edelmetaller har et redusert overpotensial for den anodiske reaksjonen sammenlignet med udopet maling. Spesielt dopet grafitt i kombinasjon med silikatbindemiddelet som beskrevet har vist seg å være en meget velegnet CP-anode i fuktig og vått miljø.

Videre kan det som nevnt påføres et impregneringsmiddel, enten samtidig med påføringen av anoden eller etter dette. Som impregneringsmiddel kan det for eksempel anvendes en lavviskositetsoppløsning av for eksempel silaner/siloksaner for å gjøre overflaten hydrofob. Siden silaner/siloksaner vil være en integrert del av silikatgelen kan det ventes en hydrofob oppførsel av lang varighet, hvilket derved vil føre til forøket levetid av anoden. En slik impregnering vil, på grunn av heftproblemer, ikke la seg utføre på en anode med et plastbasert bindemiddel.

For ytterlige å forbedre anodeløsningen som anvendes i forbindelse med foreliggende oppfinnelse kan anoden utstyres med et ionereservoar eller en "ionekappe". Årsaken til at dette er fordelaktig er at når anoden påføres over karbonatisert betong er ioneinnholdet av denne karbonatiserte betongen meget lavt, hvilket resulterer i en høy motstand i betongen like under anoden.(Som sammenligning vil for eksempel et Ti-nett innstøpes i ny ikke-karbonatisert mørtel med et langt høyere ioneinnhold under anoden.) Dette fører til at strømmen er begrenset av betongmotstanden. Som følge av den økede motstanden må spenningen økes. En høy spenning over tid vil føre til en tidlig nedbrytning av anoden på grunn av grafittoksydasjon som er avhengig av anodepotensialet. Generelt gjelder at jo høyere spenningen er, jo mer aggressiv er situasjonen ved anoden.

En annen årsak til det lave ioneinnholdet er den elektrokjemiske fjernelsen av ioner (kationer til katoden, anioner, som OH og Cl til anoden og som forlater anoden som gass) og elektroosmotisk fjernelse av vann under anoden.

Det lave ioneinnholdet blir på utmerket måte kompensert ved at påføringsmiddelet som anvendes ifølge foreliggende oppfinnelse i seg selv er elektrisk ledende. Når høye strømtettheter er påkrevet over lang tid, (som ved sterkt korrod-

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erende armering, fuktige områder) kan det påføres et ytterligere lag av et ioneholdig materiale over anoden for å tilveiebringe et reservoar av ioner. Ved hjelp av et slikt ionereservoar muliggjøres høy strømtetthet ved lave spenninger.

Et slikt ionereservoar kan for eksempel utgjøres av silikatmalinger

("murmalinger"), vannglassmørtler, sement og sementholdige produkter. Spesielt kan vannglassmørtler og sementholdige påføringer tilveiebringe et ionisk reservoar av lang varighet for å garantere forhøyede strømtettheter.

På grunn av den impregneringslignende karakteren av påføringsmiddelet som anvendes ifølge oppfinnelsen vil avskallingsproblemer ikke opptre.

De etterfølgende, ikke-begrensende, eksemplene skal belyse oppfinnelsen nærmere.

EKSEMPLER

De etterfølgende eksemplene angir forskjellige utførelsesformer av påføringsmiddelet anvendt i fremgangsmåten ifølge oppfinnelsen.

15 Eksempel 1

Det ble fremstilt et påføringsmiddel av følgende sammensetning:

175 deler kaliumvannglass K35

5 deler carbon black-dispersjon (25%)

2 deler detergent

50 deler grafitt

5 deler kalsiumhydroksyd.

Den vannglassholdige komponenten må tilsettes påføringsmiddelet noen få timer før middelet skal påføres.

Eksempel 2

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Det ble fremstilt et påføringsmiddel av følgende sammensetning:

175 deler kaliumvannglass K35

10 deler carbon black-.dispersjon (25%)

2 deler detergent

1 del "Aerosil"

4 deler kaliumhydroksyd

60 deler grafitt

11 deler natriumaluminat (5% oppløsning).

Den vannglass-reaktive komponenten , natriumaluminat, må tilsettes til blandingen få timer før middelet skal påføres.

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PATENTKRAV

- 1. Fremgangsmåte for elektrokjemisk beskyttelse av betong i utsatte miljøer, for eksempel i kontakt med, eller i nærheten av sjøvann,
- k a r a k t e r i s e r t v e d at betongen påføres et middel omfattende grafitt dispergert i et herdbart mineralsk bindemiddel, i form av vannglass eller et annet vannoppløselig uorganisk silikat, et dispersjonsmiddel samt eventuelt vanlige tilsatsstoffer, ved påsprøyting eller bestrykning, og en impregnering gjennomføres eventuelt, enten samtidig med påføringen av det ovenfor nevnte middelet eller etter dette, hvoretter det, om nødvendig, gjennomføres en etterbehandling.
 - 2. Fremgangsmåte ifølge krav 1, k a r a k t e r i s e r t v e d at middelet som påføres inneholder additiver som virker som herdemiddel.

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- 3. Fremgangsmåte ifølge foregående krav, k a r a k t e r i s e r t v e d at impregneringen gjennomføres med en lavviskøs silan/siloksan-oppløsning.
- 4. Fremgangsmåte ifølge foregående krav, k a r a k t e r i s e r t v e d at etterbehandlingen omfatter påføring av et ionisk reservoar over det påførte middelet.
- 5. Anvendelse av et påføringsmiddel omfattende grafitt dispergert i et herdbart mineralsk bindemiddel, i form av vannglass eller et annet vannoppløselig uorganisk silikat, et dispersjonsmiddel samt eventuelt vanlige tilsetningsstoffer for katodisk beskyttelse av armering i betong, samt eventuelt et ytre ionereservoar.
 - 6. Anvendelse ifølge krav 5, hvor påføringsmiddelet som tilsetningsstoff inneholder additiver som virker som herdemiddel.
 - 7. Anvendelse ifølge kravene 5-6, hvor impregneringen utføres med en lavviskøs silan/siloksanoppløsning.

8. Anvendelse ifølge kravene 5-7, hvor middelet påføres for katodisk beskyttelse av armering i betong i forbindelse med kaianlegg, broer, bropilarer og lignende.

SAMMENDRAG

Det er beskrevet en fremgangsmåte for elektrokjemisk beskyttelse av armering i betong i utsatte miljøer, for eksempel i kontakt med, eller i nærheten av, sjøvann. Betongen påføres et middel omfattende grafitt dispergert i et herdbart mineralsk bindemiddel i form av vannglass eller et annet vannoppløselig uorganisk silikat, et dispersjonsmiddel samt eventuelt vanlige tilsetningsstoffer. Påføringen foregår ved påsprøyting eller bestrykning. En impregnering gjennomføres eventuelt, enten samtidig med påføringen av middelet, eller etter dette. Om nødvendig eller ønskelig gjennomføres en etterbehandling.

Det er videre beskrevet anvendelse av påføringsmiddelet for elektrokjemisk beskyttelse av armering i betong i forbindelse med for eksempel kaianlegg, broer, bropilarer og lignende.

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(21) International Application Number: PCT/NO((22) International Filing Date: 3 February 2000 (C) (30) Priority Data: 19990509 4 February 1999 (04,02.99) (71) Applicant (for all designated States except US): PROTAS [NO/NO]; P.O. Box 75, N-3050 Mjöndalen (N) (72) Inventor; and (75) Inventor/Applicant (for US only): PRUCKNER [NO/NO]; Övre Hön Terrasse 8b, N-1370 Asker (I) (74) Agent: HANSSEN, Kari, Olaug; Bryn & Aarflot AS, F 449 Sentrum, N-0104 Oslo (NO).	03.02.00 N TECTO O). , Fran NO).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. In English translation (filed in Norwegian).
FORCEMENT IN CONCRETE	R ELE	CTROCHEMICAL CORROSION PROTECTION OF STEEL REIN-
(57) Abstract		

A method is described for the electrochemical protection of reinforcement in concrete in harsh environments, for instance in contact with, or in close proximity to, seawater. On concrete a composition comprising graphite dispersed in a curable mineralic binder in the form of water glass or another water—soluble inorganic silicate, a dispersion agent, optionally together with conventional additives is applied. The application is performed by spraying or brushing. An impregnation is optionally performed, either concurrent with the application of the composition or thereafter. If necessary a post treatment is performed. Further, the use of the composition for electrochemical protection of reinforcement in concrete in connection with, for instance, quay constructions, bridges, bridge piers and similar constructions is described.





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CONDUCTIVE MINERALIC COATING FOR ELECTROCHEMICAL CORROSION PROTECTION OF STEEL REINFORCEMENT IN CONCRETE

The present invention relates to a conductive mineralic coating to be used for electrochemical protection against corrosion of steel reinforcement in concrete. More specifically the invention relates to a method for electrochemical protection of reinforcement in concrete in harsh environments, as well as the use of a conductive coating for the protection of concrete in said environments.

It has been known for several decades that inorganic binders, such as concrete, in particular Portland cement, which has basic properties, protects metals containing iron against corrosion. Due to this protective effect against corrosion it has been possible to make reinforced concrete where the steel is embedded in concrete, and no protection has been required, for instance in the form of protective paint, on the steel.

The corrosion protecting effect of the concrete is due to the formation of calcium hydroxide during the hydratisation, leading to a pH value of 12 or more inside the concrete paste.

Because of carbonation, which means that the carbon dioxide of the air reacts with calcium hydroxide, the pH value may decrease several pH units. At pH values under 9 the steel reinforcement will start to corrode.

Corrosion is accelerated by formation of cracks in the building material as well as by the effect of chlorides from contaminated aggregates, de-icing salts, air pollution and seawater.

A method for preventing corrosion of steel in concrete is to polarise the steel cathodically (cathodic protection, electrochemical chloride removal, electrochemical realkalisation), where the steel is acting as the cathode, or the negative pole, and an external anode as the positive pole. As such external anodes use has been made of Ti- meshes, treads or rods coated with mixed metal oxides, electrically conducting asphalt, flame sprayed zinc or titanium or conductive paints. An electrically conductive paint has two important advantages. First of all it does not add extra weight to the construction, which may

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be a problem for slim constructions from a static point of view. Secondly, the conductive paint provides an excellent current distribution.

The existing paints are substantially composite materials with a polymer (acrylates, latex, polystyrene or the like) as a film forming binder (vehicle) and graphite as filler, or so-called skeleton conductor. The binder of these prior paints has practically no conductivity, but is present in the material as a binder adhering to the concrete. The anode is thereby composed of fibres or grains of graphite embedded in an insulator. The conduction will proceed via these points of contact and one would therefore expect a considerable strain at the interphase graphite/graphite. This will to a very considerable degree limit the conductivity of the anode, which has to be compensated by an increased number of connection points (often called "primary anodes"). In addition, the high transfer resistance from such an anode to the concrete has the effect that a higher voltage will be required. This leads to electrolysis and oxidation of graphite causing loss of adhesion due to acidification of the concrete subbase and decreased conductivity of the paint, thus the anode will "die". It should be added that synthetic binders are diffusion preventing and may therefore not be regarded as durable in harsh environments. The paint will further lose its adhesion to the concrete subbase due to the electrochemical reactions taking place at the inter-phase between concrete and paint, which lead to failure of the electrochemical treatment.

Major corrosion damages are occurring on concrete in harsh, or extreme, environments, as for instance in contact with, or in close proximity to, seawater. In environments like this new requirements are also placed on the anode materials, since also these materials will be subject to extensive corrosion. As an example mention may be made of a quay construction prone to corrosion of the reinforcement. The only possibility for solving this problem has been cathodic protection, preferably with Ti meshes embedded in shotcrete, installed under the quay. This is a cumbersome and expensive procedure. Delamination of these layers is also taking place to a considerable degree. It has been proven to be impossible to use the previously known paint systems under such wet or humid conditions. This is due to the fact that extensive delamination and/or blistering will take place due the humidity

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present, and it will often be problematic to attain sufficient adhesion already during the initial application of the paint film.

The prevailing opinion within the art is therefore that conductive paints are not applicable under these harsh and humid conditions. At present the embedding of conductive meshes is thus regarded as the only, albeit unsatisfactory, solution.

The purpose of the present invention is to provide a new and simple solution to this problem, more specifically to provide an easily applicable, mechanically and electrochemically stable anode embodiment which also functions well in humid environment and in close proximity to, or in contact with, sea water.

For the solution of this problem the inventor has realised the necessity of avoiding film forming coatings, and has thereby developed a very simple and suitable system.

It is known that silicate based mineralic paints react with the substrate (plaster, concrete, stone etc.) by petrification. This means that the water soluble silicates penetrate the mineralic substrate upon which they have been applied and form a chemical micro-crystalline bond with said substrate, in contrast to film-forming paints which form a surface skin.

Saunders describes, in US patent No. 4.035.265, a conductive paint for application on walls and the like for heating purposes. The paint composition contains carbon particles together with flakes of graphite, and further a curable binder such as an inorganic silicate binder, an organic ammonium silicate binder or for instance a resin binder, which is soluble in organic solvent. Due to the intended use as heat source this paint contains large amounts of graphite/ carbon particles. There are also considerable further differences, to be described in greater detail below, between this system and the present invention.

The present invention thus provides a method for electrochemical protection of reinforcement in concrete in harsh environments, for instance in contact with, or in close proximity to, sea water, whereby a composition comprising graphite dispersed in water glass or another inorganic silicate, a dispersing agent and optionally conventional additives, is applied to the

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concrete by spraying or painting, and optionally an impregnation is carried through, either concurrent with, or after, the application of the said composition. Optionally a post treatment may also be performed.

Since the method according to the invention does not lead to the formation of any film, but rather an impregnation, the above mentioned problems connected to adhesion, delamination and blistering do not occur. The mineralic composition will penetrate the outer layer of the concrete and form a gellike material in the pores and on the concrete surface, and will therefore, when the water evaporates, adhere strongly to the surfaces of, for instance, concrete masonry and natural stone. The transfer resistance between anode and concrete will thus be as low as possible.

When the cathodic protection installation is energised the voltage field that arises will entail migration of ions which leads to further curing and strengthening of the anode. Due to the strength of the cured coating the graphite particles will be totally immobilised and function as a well-established skeleton whereby a highly conductive anode for electrochemical treatments is obtained. As a consequence the method according to the present invention may be operated at higher current densities than the previously known paint coatings. The higher current densities will further be attained at lower voltage than with known types of anodes. This will strongly affect the lifetime of the anode in a positive direction.

Since the solution/dispersion of the mineralic compounds used in the composition are highly alkaline the delamination effects due to acidification of the inter-phase coating/concrete caused by the electrochemical process at the anode are strongly reduced. An anode according to the state of the art with latex or acrylic binder will, in contrast, lose adhesion over time due to this process. This feature is of major importance since acid will be generated at the anode/concrete interface. With the alkaline coating according to the present invention a reservoir against acid formation is obtained, which is very desirable for preventing delamination of the conductive paint due to acidification, especially at the beginning of any cathodic protection treatment where higher protective current densities are needed.

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Another positive effect caused by this type of anode for cathodic protection is that the electrical field will draw alkali ions from the coating composition into the concrete by electrophoretic movement. This leads to an increased degree of polymerisation of the silica gel, which thereby will become increasingly petrified and resistant. After a certain time a completely insoluble matrix of silicate hydro-gel will be formed as binder. The silicate composition used in the method according to the invention is thus excellently suitable as anode in the cathodic protection of very humid structures, such as for instance under quay installations, harbour installations or bridge piers, where conventional paints up to now have failed.

The coating composition may, in the method according to the invention, be applied by simple spraying on the surface of the concrete, for instance with conventional paint spraying devices or brushed on the surface by using conventional equipment.

As mentioned earlier, conventional additives may, if desired, be added to the coating composition used. Among these curing agents may also be added. As curing agents use may for instance be made of phosphates of aluminium, iron, zinc, lead and so forth, polyvalent esters or ammonium, amine or amide compounds. As mentioned earlier the current through the applied impregnation itself will effect sufficient curing. Situations may arise, however, where addition of a curing agent may be advantageous, for instance before the passing of current is possible or before other protection is in place.

According to one possible embodiment of the present invention a catalyst may be added to the coating composition. As catalyst use may be made of precious metals, heterocyclic compounds with interstitial metal atoms and so forth. It has been observed that doping of the graphite with precious metals inhibits oxidation of the graphite. The coating composition containing graphite doped with precious metals has a reduced overpotential for the anodic reaction compared to undoped paint. In particular doped graphite in combination with the silicate binder as described above has proven to be a very suitable CP anode for humid or wet environments.

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An impregnation agent may further be applied, either concurrent with the application of the anode or thereafter. As an impregnating agent use may for instance be made of a low viscosity solution of for instance silanes/ siloxanes in order to make the surface hydrophobic. Since silanes/siloxanes will be an integrated part of the silica gel a long lasting hydrophobic behaviour may be expected, leading to an increased lifetime for the anode. A similar impregnation will, due to adhesion problems not be possible on a plastic based binder.

In order to further perfect the anode solution in connection with the present invention the anode may be supplied with an ionic reservoir or an "ionic mantel". This is advantageous because when the anode is applied over carbonated concrete the ion content of this carbonated concrete is very low, which implies a high resistance in the concrete close to and underneath the anode. (As a comparison a Ti mesh will for instance be cast into new uncarbonated concrete with a far higher ionic content under the anode.) The current will thus be limited by the resistance of the concrete. As a consequence of the increased resistance the voltage will have to be increased. A high voltage will, over time, result in a premature breakdown of the anode due to graphite oxidation, which is dependent on the anode potential. In general, the higher the voltage, the more aggressive the situation at the anode.

Another reason for the low ionic content is the electrochemical removal of ions (cations to the cathode and anions, as OH⁻ and Cl⁻ to the anode and which leaves the anode as oxygen and chlorine gas) and electro-osmotic removal of water under the anode.

The low ionic content is compensated in an excellent way since the coating composition used according to the present invention itself contains ions. When high current densities are required over a long time,(as in the case of strongly corroding reinforcement, humid areas) a further layer of ionic material may be applied over the anode in order to provide a reservoir of ions. By such an ionic reservoir high current densities by low voltages are made possible.

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Such an ionic reservoir may for instance be constituted by silicate paints ("concrete paints"), water glass mortars, cement, and cementitious products. In particular water glass mortars and cementitious coatings may provide an ionic reservoir of long durability in order to secure elevated current densities.

Due to the impregnating character of the coating used according to the invention delamination will not take place.

The following, non-limiting examples will illustrate the present invention.



EXAMPLES

The following examples describe different embodiments of the coating composition used in the method according to the invention.

Example 1

A coating of the following composition was prepared:

175 parts of potassium silicate solution K35

5 parts of carbon black dispersion (25%)

2 parts of detergent

50 parts of graphite

5 parts of calcium hydroxide.

The water glass containing component must be added to the coating composition a few hours before the coating is to be applied.

Example 2

A coating of the following composition was prepared:

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175 parts of potassium silicate solution K35

10 parts of carbon black dispersion (25%)

2 parts of detergent

1 part of "Aerosil"

3 parts of calcium hydroxide

60 parts of graphite

11 parts of sodium aluminate (5% solution).

The water glass reactive component, the sodium aluminate, must be added to the composition a few hours before the coating is to be applied.

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CLAIMS

- 1. A method for electrochemical protection of concrete in harsh environments, for instance in contact with, or in close proximity to sea water, characterised in that a coating comprising graphite dispersed in a curable mineralic binder, in the form of water glass or another water soluble inorganic silicate, a dispersion agent optionally together with conventional additives, is applied to the concrete, either by spraying or brushing, and an impregnation is optionally carried through, either concurrent with the application of the above agent or thereafter, and, if necessary a post treatment is carried through.
- A method according to claim 1,
 c h a r a c t e r i s e d i n that the coating composition comprises additives
 which function as curing agents.
- 3. A method according to the preceding claims, characterised in that the impregnation is performed with a silane/siloxane solution of low viscosity.
- 4. A method according to the preceding claims, characterised in that the post treatment comprises application of an ionic reservoir over the applied coating.
- 5. Use of a coating composition comprising graphite dispersed in a curable mineralic binder, in the form of water glass or another water soluble inorganic silicate, a dispersing agent, optionally together with conventional additives for cathodic protection, as well as optionally an outer ionic reservoir, for the protection of concrete against corrosion.
- 6. Use according to claim 5, wherein the composition, as additives, contains additives which function as curing agents.



- 7. Use according to claims 5-6, wherein the impregnation is carried out with a silane/siloxane solution of low viscosity.
- 8. Use according to claims 5-7, wherein the composition is applied for cathodic protection of reinforcement in concrete in connection with quay constructions, bridges, bridge piers and similar constructions.